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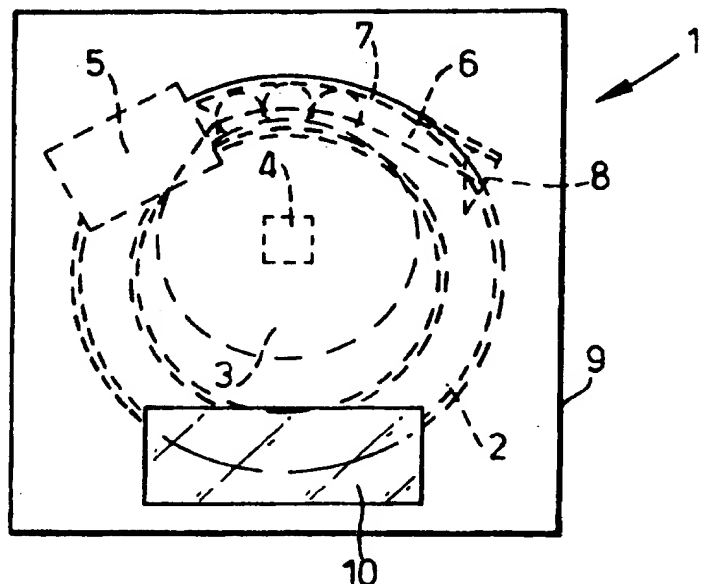
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Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: VEHICLE OCCUPANT RESTRAINT SYSTEMS POWERED BY GAS GENERATING COMPOSITIONS

(57) Abstract

A vehicle occupant restraint system which incorporates a gas generating composition comprising: (i) nitroguanidine; (ii) an oxidising agent; (iii) an oxide of silicon or aluminium, a mixed oxide of silicon and aluminium, or a silicate. The vehicle occupant restraint system may comprise an air bag or a seat belt pretensioner.



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VEHICLE OCCUPANT RESTRAINT SYSTEMS POWERED BY GAS
GENERATING COMPOSITIONS

This invention relates to vehicle occupant restraint systems which are
5 powered by gas generating compositions.

Vehicle occupant restraint systems have now become widely available.
Typical of such systems are inflatable air bags and seat belt pre-tensioners. In
both of these applications there is a requirement for compositions which can
generate gas very rapidly in the event of a collision. In the case of an air bag the
10 composition is required to inflate the bag, and in the case of a seat belt
pre-tensioner it provides the motive force to operate the pre-tensioning
mechanism. Such compositions are generally of a pyrotechnic nature and are
ignited by means of an electrically or mechanically initiated igniter.

A variety of gas generating compositions have been proposed hitherto,
15 among which may be mentioned sodium azide-based compositions, single or
double-based propellant compositions, and aminotetrazole-based compositions.
In practice, however, none of these compositions have been found to be wholly
satisfactory.

Sodium azide-based compositions produce only approximately 50% of their weight as nitrogen gas; the remaining 50% by weight comprises particulate solid products which do not contribute to, for example, the inflation of an air bag, and which have to be filtered out of the stream of hot gas. Sodium azide itself is extremely toxic, expensive to produce and difficult to dispose of. It is, however, widely used because the propellant gas evolved is almost entirely nitrogen and thus itself is of low toxicity.

Single and double-based propellants have a limited useful lifetime when stored at high temperatures. Some concern has therefore been expressed about the use of these propellants, which contain nitrocellulose, in air bags to be installed in cars driven in hot climates, for example desert regions of the USA or Australia, since they may not be able to provide a 15 year service life. In addition, carbon monoxide makes up approximately 33% by weight of their products of combustion, and this gas is relatively toxic. Single and double-based propellants do, however, have a major advantage in that more than 99.5% of their weight is converted to gas and little provision needs to be made for the filtering out of solid products.

Compositions based on aminotetrazoles and derivatives of aminotetrazoles (for example 5-aminotetrazole) are superior to single and double-based propellants in stability and to sodium azide in toxicity. The percentage conversion to gas is approximately 60 - 70% by weight, of which most is

nitrogen and very little is carbon monoxide, although up to 10% is carbon dioxide. The compositions generate a smaller weight of solid particulate products of combustion than sodium azide compositions, but more than that generated by single or double-based propellants. The start-up cost of manufacture of 5 aminotetrazoles is, however, relatively high and their advantages are not sufficient to outweigh this factor.

It will be apparent from the above that there is a need for a gas generating composition of low toxicity, having combustion products also of low toxicity, which has a high percentage of its weight converted to gas on ignition, which is 10 stable at elevated temperatures for very long periods of time and which can be produced, handled and disposed of relatively economically.

According to the present invention there is provided, for use in a vehicle occupant restraint system, a stable gas generating composition comprising nitroguanidine.

15 The present invention provides a vehicle occupant restraint system which incorporates a gas generating composition comprising:

- (i) nitroguanidine;
- (ii) an oxidising agent; and
- (iii) an oxide of silicon or aluminium, a mixed oxide of silicon and 20 aluminium, or a silicate.

The nitroguanidine component (i) of the compositions of the invention is commercially available under the trivial names "Picrite" or "NQ". Preferably it is used in its alpha form, which comprises long, thin, crystalline needles. It is of relatively low toxicity and can be produced relatively cheaply.

5 The oxidising agent component (ii) used in the compositions of the present invention is also preferably of low toxicity and has combustion products of low toxicity. Suitable oxidising agents include, for example, nitrates, and particularly nitrates of metals, more particularly alkali and alkaline earth metals, especially sodium, potassium and strontium nitrate.

10 Other oxidising agents such as potassium perchlorate may also be used, either alone or in combination with a metal nitrate.

Oxidising agents comprising bismuth, barium, vanadium and chromium salts are not preferred because of the toxicity of the compounds themselves, or of their combustion products, or both.

15 Component (iii) of the composition comprises an oxide of silicon or aluminium, a mixed oxide of silicon and aluminium, or a silicate. Preferred materials are those which are capable of reacting with the oxide or oxides produced by the combustion of the oxidising agent component, to form silicates,

aluminates, or mixed compounds thereof. Suitable compounds for the third component include silica, alumina, silicoaluminates, diatomaceous solids and silicate-containing minerals. The third component is preferably present in a finely divided state.

5 The compositions of the present invention preferably comprise from 50 to 67% by weight of nitroguanidine, from 30 to 45% by weight of oxidising agent, and from 3 to 5% by weight of a silicon and/or aluminium containing compound, based on the total weight of the composition.

Preferred compositions according to the invention are relatively
10 non-toxic, and can convert over 78% of their weight to gas, of which less than 0.02% is carbon monoxide. The preferred compositions are stable at elevated temperatures, for example up to 200°C.

The vehicle occupant restraint system according to the invention can be an
air bag used as an automotive safety restraint, or a seat belt pre-tensioning
15 device.

A preferred embodiment of a composition for incorporation in a vehicle occupant restraint system according to the invention is illustrated in the following example:

EXAMPLE

A solid gas generating composition according to the invention is prepared by mixing 58.1% by weight of nitroguanidine, 37.9% by weight of particulate sodium nitrate, and 4% by weight of silica in a blender (Composition I). The composition is found to be stable at 105°C for a period of 6 months.

Computer modelling has predicted the following properties of composition I on combustion:

Gas Yield	29.8 molc/Kg
Weight Solid Products	21.5%
10 Conversion to Gas	78.5%
Density	1.9g/cc

Computer modelling has also predicted the following gaseous products of combustion (in mole fraction) of Composition I.

Carbon monoxide	0.00025
15 Carbon dioxide	0.15446
Hydrogen	0.00024

Vaporised Water	0.35794
Nitrogen	0.43337

The invention will now be further described by way of example only with reference to and as illustrated in the accompanying drawings in which:

5 Figure 1 shows, in side elevation, an embodiment of a vehicle occupant restraint system according to the invention, in the form of a seat belt pretensioner drive mechanism;

Figure 2 shows the pretensioner of Figure 1 in top elevation;

Figure 3 shows the pretensioner of Figures 1 and 2 in side elevation in
10 an enlarged scale with parts broken away to illustrate the mode of operation;

Figure 4 shows the pretensioner of Figures 1 to 3 in end elevation again with parts broken away to show the mode of operation;

Figure 5 shows a scrap view in section of the gas-generating mechanism of the pretensioner shown in Figures 1 to 4; and

15 Figure 6 shows another embodiment of a vehicle occupant restraint system according to the invention, in the form of an inflator assembly for an air bag.

Referring firstly to Figure 1, the pretensioner illustrated generally at 1 comprises a curved pressure tube 2 which is coiled around a drive wheel 3
20 attached to a shaft 4. The pressure tube 2 is mounted eccentrically of the axis of the drive wheel 3 and has a diameter of curvature slightly greater than the wheel. The tube 2 has a closed end, at which there is situated a cap enclosing a

gas-generating mechanism 5, and an open end which is cut back, as illustrated by the broken line 6, to form an open-sided channel 7. At the end of the channel 7 there is provided a projecting arrest member 8. As can be seen from Figure 2, the curved pressure tube 2 describes approximately $1\frac{1}{2}$ turns about the drive wheel 3.

5 The pretensioner is enclosed in a collection chamber 9, which may comprise the whole or part of the seat belt retractor housing, the chamber 9 having a clear panel 10 for viewing the interior thereof.

Referring now to Figure 3, which depicts the pretensioner in operation, a row of metal balls 11 are illustrated passing along the channel 7 of the pressure tube 2. There may be, for example, from 30 to 50 of such balls 11 in the pressure tube 2. The balls 11 have a diameter slightly less than the internal diameter of the tube 2 and are freely moveable therein. The drive wheel 3 is provided with a series of circumferential indentations 12 about its periphery, which are spaced apart by a distance such that when adjacent balls 11 are located in the

15 indentations their surfaces are just touching. The arrangement is shown again in Figure 4 which also shows the drive shaft 4 which is attached to the take-up reel of a seat belt retractor (not shown).

Figure 5 shows a detail of the gas-generating mechanism 5. A pyrotechnic gas-generating composition 13 in accordance with the invention (for example Composition I) is packed into a pressure-resistant plug 14 firmly

20 mounted at the end 15 of the pressure tube 2. The pyrotechnic composition 13 is

ignited by an electronic igniter (not shown) which is activated by a deceleration sensor (not shown). A felt plug 16 is positioned at the end 15 of the pressure tube 2 and serves as a limit member for the travel of the row of balls 11.

In the rest, or inactive, position of the pretensioner, the balls 11 are 5 confined within the pressure tube 2 by a rigid foam 17 which is injected into the pressure tube 2 after the balls have been inserted and which solidifies to retain the balls 11 in the pressure tube. The plug 16 prevents the foam from reacting the pyrotechnic composition. With the balls 11 retained in the tube 2, the drive wheel 3 and shaft 4 are able to rotate freely with the take-up reel of the seat belt 10 retractor. The ball retaining means may alternatively comprise, for example, a frangible plug, or a spring means, which is compressed as the balls are ejected from the pressure tube.

In the event of an imminent collision, the deceleration sensor activates the electronic igniter which in turn sets off the pyrotechnic gas-generating 15 composition 13. The volume of gas generated by the composition 13 is sufficient to displace the felt plug 16, and propel the row of balls 11 at considerable speed along the pressure tube 2. The foam 17, of course, disintegrates as the balls are ejected from the pressure tube 2. When the balls reach the open channel 7 they come into contact with the indentations 12 on the drive wheel 3 and cause the 20 drive wheel 3 and drive shaft 4 to rotate at high speed. The drive shaft rotates the take-up reel of the seat belt retractor causing retraction of the seat belt by the desired amount.

The path of the balls is tangential to the circumference of the drive wheel 3 and as they fly off they each come into contact with the arrest member 8 at the end of the open channel 7 and suffer a substantial deceleration. This prevents the balls from damaging the wall of the collection chamber 9. The 5 pretensioner is preferably enclosed within the housing of the seat belt retractor, which comprises the collection chamber 9, and as the balls are ejected from the open channel 7, they collect in the bottom of the housing from where they can be viewed through the clear panel 10 to provide a visual check on whether the pretensioner has been activated. After use, they can be recovered and reused 10 with a fresh charge of pyrotechnic composition as appropriate.

After the last ball has left the periphery of the drive wheel 3 there is no further force acting on the drive wheel which is then locked in position by the seat belt retractor lock. When the vehicle has come to a halt, the seat belt retractor lock is released and the seat belt can again be used normally.

15 A further embodiment of vehicle occupant restraint system according to the invention is illustrated in Figure 6, which shows an inflator assembly for an air bag.

The inflator assembly, illustrated generally at 21, comprises a generally cylindrical housing 22, having an integral peripheral flange 23. The flange 23 has 20 means (not shown) for attachment to the fascia, steering wheel or steering

column of a vehicle. Within the housing 22 are packed pellets 24 of composition 21, which surround an igniter and booster 25 which is sealed into the housing 22. Electrical lead wires 26 are connected to the igniter and booster 25. The flange 23 is turned back on itself to give first and second clamping surfaces 27, 28 between 5 which are clamped the edges of an air bag mouth (not shown). The air bag is omitted for clarity, but would be folded around, and clamped by its edges to, the flange, to make an airtight seal with the inflator assembly.

Mounted on the housing 22, is a cap member 29 provided with an annular particle filter 30, in the form of a skirt. The filter 30 and cap member 29 are 10 firmly fastened to the housing 22 and, in operation are positioned in the mouth of the air bag.

In operation, the electrical lead wires are connected to an electrical control unit (not shown) which, when a rapid deceleration is detected, electrically activates the igniter and booster 25. The igniter and booster 25 ignites the pellets 15 of Composition I which quickly evolve large quantities of gas. The gas passes through the particle filter 30 and into the air bag, causing rapid inflation. *

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this 20 application and which are open to public inspection with this specification, and

the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment. This invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A vehicle occupant restraint system which incorporates a gas generating composition comprising:
 - (i) nitroguanidine;
 - 5 (ii) an oxidising agent;
 - (iii) an oxide of silicon or aluminium, a mixed oxide of silicon and aluminium, or a silicate.
2. A vehicle occupant restraint system according to Claim 1, in which the oxidising agent comprises a metal nitrate.
- 10 3. A vehicle occupant restraint system according to Claim 1 or 2, in which the oxidising agent comprises an alkali metal nitrate.
4. A vehicle occupant restraint system according to any of the preceding claims, in which component (iii) comprises silica.
5. A vehicle occupant restraint according to any of the preceding claims, in
15 which component (iii) is present in a finely divided state.

6. A vehicle occupant restraint system according to any of the preceding claims, in which the gas generating composition comprises:

from 50 to 67% by weight of nitroguanidine;

from 30 to 45% by weight of an oxidising agent; and

from 3 to 5% by weight of a silicon and/or aluminium

5

containing compound.

based on the total weight of the composition.

7. A vehicle occupant restraint according to any of the preceding claims, in which the gas generating composition comprises nitroguanidine, sodium nitrate, and silica.

10

8. A vehicle occupant restraint system according to any of the preceding claims, comprising a gas generating composition substantially as described in the Example.

9. A vehicle occupant restraint system which incorporates a gas generating composition substantially as hereinbefore described.

15

10. A vehicle occupant restraint system according to Claim 9, in which incorporates a gas generating composition according to any of Claims 1 to 9.

11. A vehicle occupant restraint system according to Claim 9 or 10, in which the gas generating composition is contained within an inflator assembly connected to an air bag adapted to be inflated by the gas generating composition.
- 5 12. A vehicle occupant restraint system substantially as hereinbefore described.
13. A vehicle occupant restraint system which comprises an air bag and a gas generating pyrotechnic composition comprising nitroguanidine whereby the air bag may be inflated.
- 10 ⁴ 14. A vehicle occupant restraint system which comprises an inflator assembly for an air bag, the inflator assembly comprising a gas generating pyrotechnic composition comprising nitroguanidine.

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Fig.1.

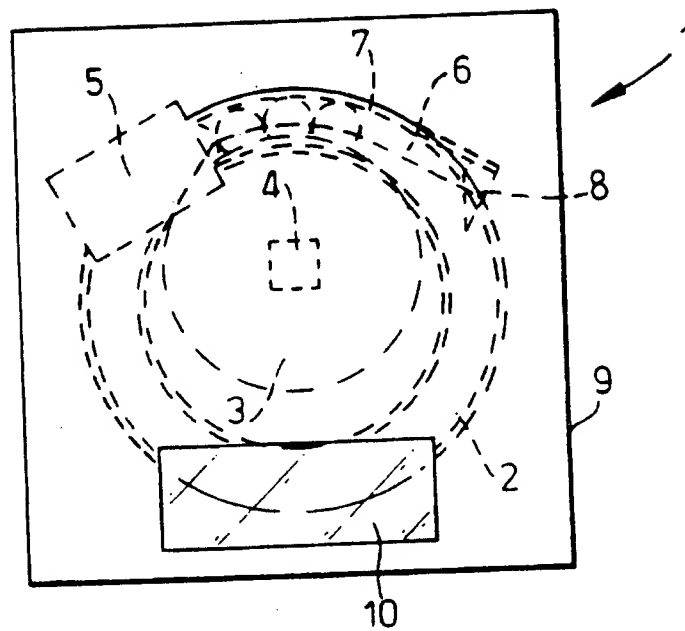
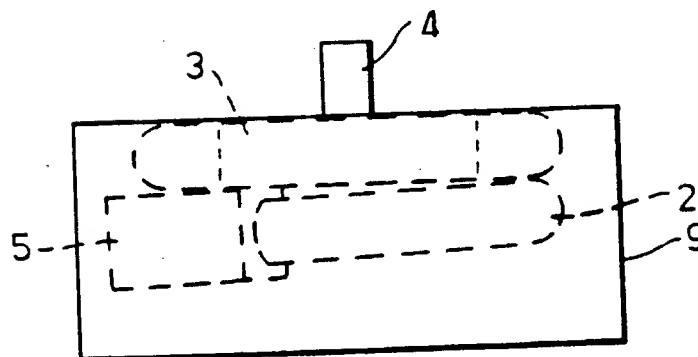


Fig.2.



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Fig.3.

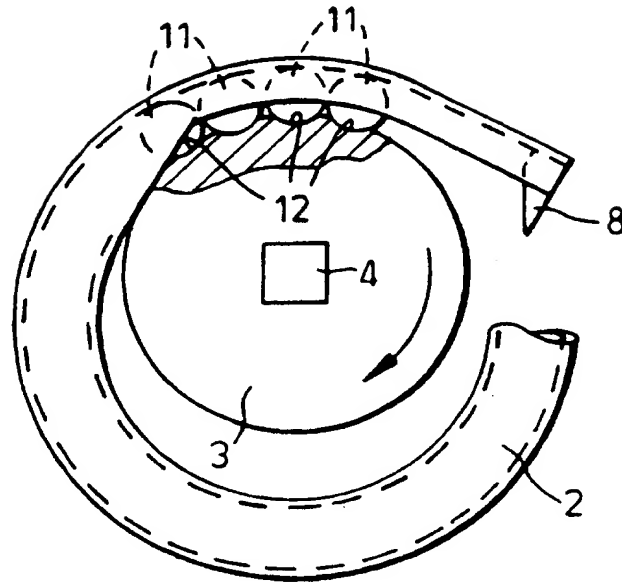


Fig.4.

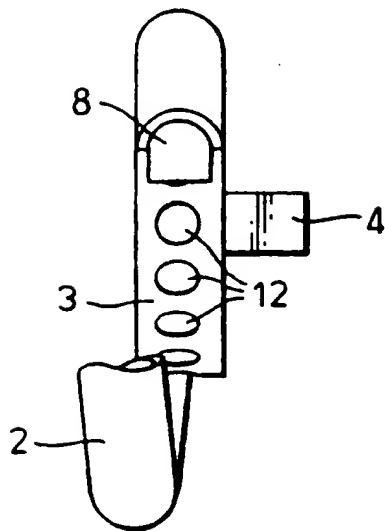


Fig.5.

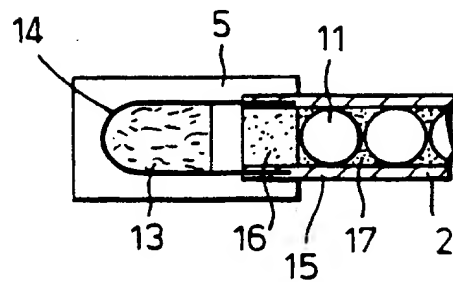
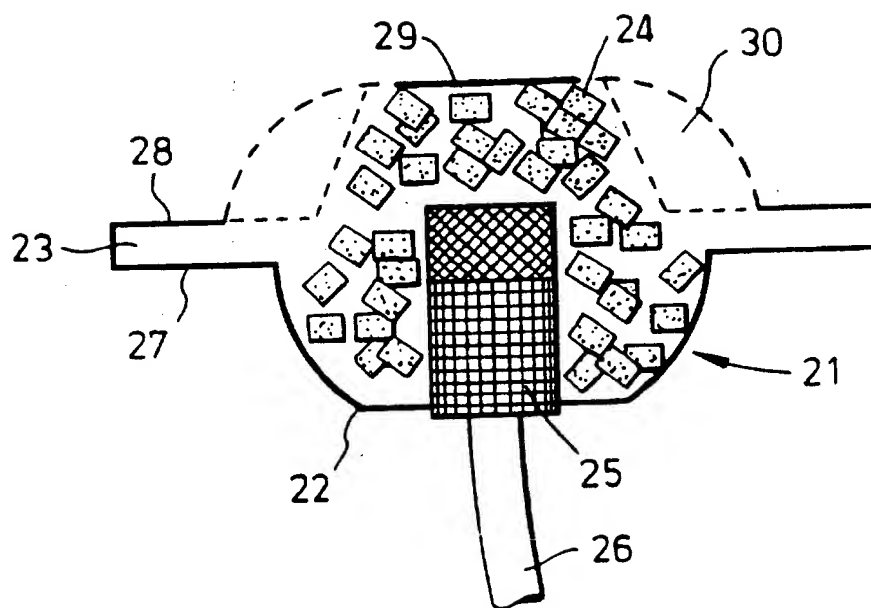


Fig.6.



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 96/00328

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C06D5/06 C06B25/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C06D C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,U,94 16 112 (CONTEC-CHEMIEANLAGEN GMBH) 15 December 1994	1-5, 9-13, 15
Y	see page 2, line 20 - line 30; claims; table 1 ---	6-8
Y	DE,C,884 170 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 23 July 1953 see page 3, line 73 - line 94; claims ---	6-8
Y	US,A,5 125 684 (R.V. CARTWRIGHT) 30 June 1992 see claims ---	6-8
Y	DE,A,44 12 871 (NOF CORP.) 20 October 1994 see page 4, line 1 - line 30 see page 7, line 60 - page 9, line 46; claims 15-20 --- -/-	6-8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category	Citation of document, with indication, where appropriate, of the relevant passages	
A	EP.A,0 607 446 (NIPPON KOKI CO., LTD. ET AL.) 27 July 1994 see page 3, line 33 - line 54; claims; table 3	1-15
Y	----- J. QUINCHON: "Poudres, Propergols et Explosifs" 1987, TECHNIQUE & DOCUMENTATION-LAVOISIER , PARIS, FRANCE XP002005003 see page 237 - page 239 -----	6-8

INTERNATIONAL SEARCH REPORT

International Application No

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